Coupled effect of feedstock and pyrolysis temperature on biochar as soil amendment

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***Abstract*—Thailand is an agricultural country based. A strategy to use biomass is to produce biochar which has original properties that make it a valuable soil amendment. This study investigated the effect of pyrolysis temperatures (350 and 550 °C) using difference types of biomass, including coconut shell, eucalyptus, and sugar cane. The link between biochar properties and its function as soil fertilizer is used to give a definition for biochar quality. Results shown the highest surface area and pore volume were found for coconut shell at 550°C. Biochar pH values were all alkaline whatever the temperature. The first indication of the suitability of soil fertilizer is the nutrient content which has been found the highest for sugar cane at 350°C. The highest ratio (P+K):N, the better the release of the nutrient content. Finally, biochar quality will be driven by raw materials and pyrolysis conditions.**

***Keywords*— Biomass, Biochar, Pyrolysis, Soil amendment**

I. Introduction

Pyrolysis is the most common method to produce biochar. Generally, biochar is a production of pyrolysis that is often carried out under low temperatures that lead to a partially carbonized product [1]. Biochar can be produced from various raw materials under different processing conditions such as temperature, heating rate, and particle size of raw material [2]. Biochar has been widely used in many applications, especially in a soil amendment [3] due to its physicochemical characteristics [4].However, production of high-quality biochar is still inadequate as some parameters influencing biochar production are not well known or comprehensive yet.

The chemical characteristics of biochar can be highly variable depending on feedstock composition and pyrolysis conditions. Fig.1. summarizes the percentage of publications [5-9] dealing with pyrolysis parameters effecting the biochar quality. Pyrolysis temperature and feedstock are the most investigated with 46% and 30% respectively.

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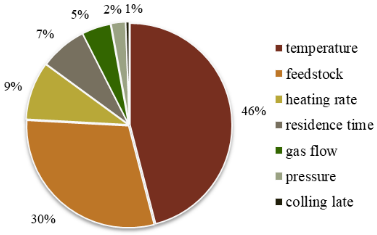

Fig.1. Percentages of the biochar studies and pyrolysis parameters investigated

According to the Fig.2 slow pyrolysis represents the main process investigated to produce biochar (78%).

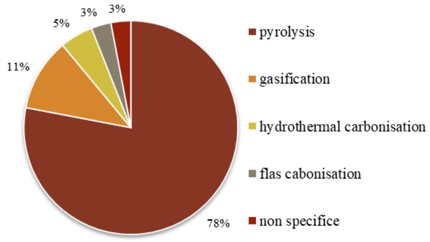

Fig.2. Percentages of the publications dealing with biochar production processes

This study aims to investigate the influence of both pyrolysis conditions and feedstock composition on biochar quality. As a first step, experiments will be conducted in a lab-scale reactor to produce biochar before characterization. These biochar characteristics will be used as an indicator to identify the optimum pyrolysis temperature for producing biochar as a soil amendment. Our expected to give a guideline to product biochar with quality for soil.

II. Methodology

A. Raw materials

Sample collection was conducted based on agricultural wastes in Thailand to produce biochar under the pyrolysis parameters controlled. The experiments were run with different raw materials, including coconut shells (CS), eucalyptus (EC), rice straw(RS) and sugar cane leaves (SC) shown in Fig.3 Biomasses were pyrolyzed as it stands, no crushing or sieving has been performed to reduce particle size[3]. Prior to the experiments, all the samples were dried.

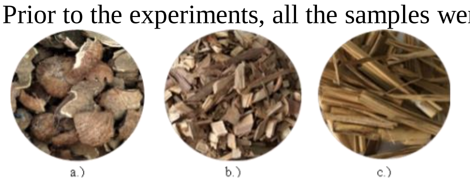

Fig.3. Raw materials: a.) coconut shells (CS), b.) eucalyptus (EC), and c.) sugar cane leaves (SC)

B. *Biochar production*

Experiments were conducted in a macro TG reactor [10]. About 30-100 g of sample was placed in a basket located in the middle of the reactor. It had to be ensured that there was no oxygen present during pyrolysis.

Experiments will be conducted low at 350°C and high (550°C) temperatures. The experiment assumes pyrolysis temperatures are common in traditional technologies operated by farmers. For each test, we will apply a heating rate at 5 °C/min and holding time 1 hour after cooling down to the room temperature, the biochar is weighted and characterized. Table I summarized the list of raw materials used as well as the experimental conditions.

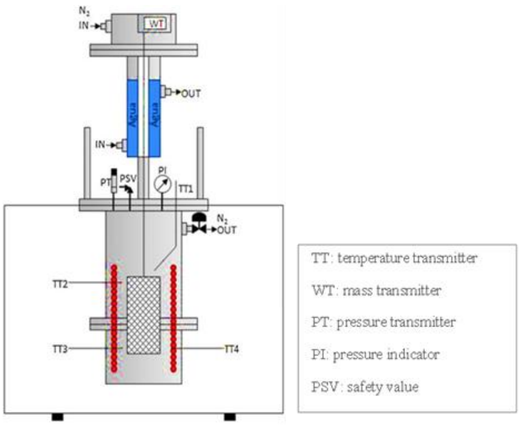

Fig.3. Macro TG reactor [10]

Table I Experimental Conditions and Notations

Raw material	Experimental conditions 350 °C	Experimental conditions 550 °C
Coconut shell (CS)	CV350	CV550
Eucalyptus (EC)	EC350	EC550
Sugar cane leaves (SC)	SC350	SC550

C. *Characteristics analysis*

In this study for measuring the surface area, pore volume and pore size by Brunauer-Emmett-Teller (BET) instrument using nitrogen gas. Biochar pH values were measured by using a ratio of 1.0 g of biochar in 20 ml deionized water. Then the samples with modification that the time on the shaker was increased to 1.5 hrs [11]. The elemental analysis was analysed by use of an elemental analyser (Thermo FlashEA 1112). Assessment of ash content was performed by X-ray fluorescence (XRF) spectrometry, a rapid method used to determine the composition of biomass ash.

III. EFFECT OF PYROLYSIS TEMPERATURE AND FEEDSTOCK TYPES ON BIOCHAR

A. *Surface area, total pore volume and average pore diameter of biochar*

An important soil characteristic, as it influences all of essential functions for fertility, is surface area. Sandy soil has very low specific about 0.01 m^2/g to 0.1 m^2/g. Its surface area relates to the limited capacity to store water and plant nutrients. The surface area is ranging from 5 m^2/g to 750 m^2/g resulting in a high total water-holding capacities. Generally, biochar specific surfaces are higher than sand and can be higher or comparable to the clay. When biochar is added to soil, the amendment will therefore cause a net increase in the total soil specific surface[12].

The surface area, total pore volume, and pore diameter of biochar were characterized by BET method. As shown in figure 5 and 6, as the pyrolysis temperature was increased from 350 to 550 °C, the surface area and total pore volume increased significantly mainly due to removal of volatile matter during pyrolysis process. The specific area of biochar ranges from 125m^2/g to 462m^2/g for SC350 and CS550 respectively. Figure 7 compiles data demonstrating the relationship between total pore volume and surface area. This provides evidence that the distribution in the total pore volumes makes the greatest contribution to total surface area. The results showed that the surface area was comparable to clay's surface area as mentioned in the literature review. Surface area and porosity of biochar are related to water retention and CEC in soils [1, 13, 14]. Therefore, the biochar produced at 550°C has a higher surface area and pore volume than biochar produced at 350°C. For soil amendment, increased water capacity, and CEC in soil. It is necessary to use biochar production at high temperature rather than at lower temperature.

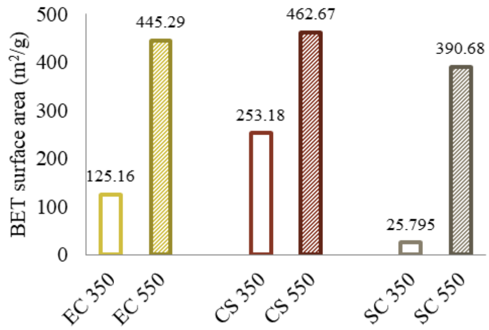

Fig.5. BET surface area of biochar

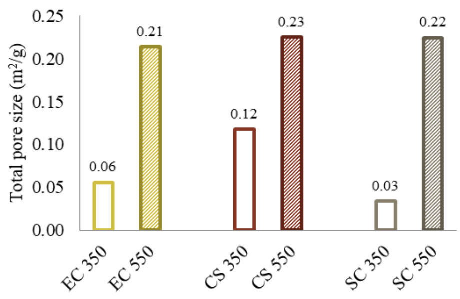

Fig.6. Total pore volume of biochar

The pore size of biochar will also be of emphasis to their behavior in soil amendment. The pore size of this study will be divided into micropores and mesopores. The micropores as all pores are of diameter less than 2 nm. For the average pore size approximately 2 to 50 nm can be assumed, which describes a mesoporous structure [12, 15, 16]. The Figure 8 shows the average pore diameter of biochar. It ranges from 1.77 nm to 5.22 nm. Most of biochar has micropore size including EC350, EC550, CS350 and CS550. Microspores contribution is considerable to the biochar's surface area, as well as the high adsorptive capacities for molecules of small dimensions (like gas and common solvent) is their accountability too. Biomass produced from eucalyptus, and coconut shells has shown that different temperatures do not affect the average pore diameter of biochar, because products from both temperatures are similar to average pore diameter. Biochar produced from sugar cane (SC350) had a higher pore size than other products. That is an interesting point for future research, as the structure of raw materials may affect the properties of biochar.

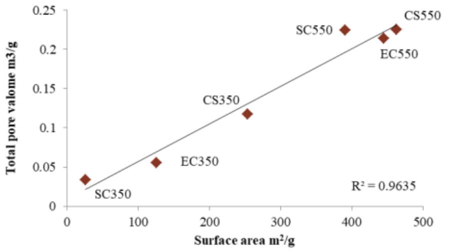

Fig.7. Relationship between total pore volume and BET surface area

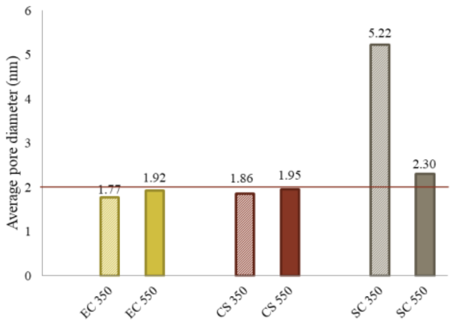

Fig.8. Average pore diameters

B. *pH values*

Applying biochar to optimize soil pH is an option [17].The pH value of raw materials and biochar produced under different pyrolysis temperatures are given in Figure 9 The pH of the biochar's production was between 9.75 and 10.77, which is close to the value report of biochar produced from agriculture waste [18]. The range of biochar has shown that biochar is alkaline, which is in line with what the literature review has supported[17]. For raw materials the pH values ranged from 4.46 to 7.38. The highest pH value was found in sugarcane (SC) and the lowest was found in eucalyptus (EC) with 7.38 and 4.46, respectively. From both pyrolysis temperatures the highest pH value was represented in biochar produced from sugarcane. At pyrolysis temperature 350 °C the highest pH is SC350 with pH 10.51. As with 550 °C, SC550 °C has shown the highest pH value is 10.77. The Figure 9 summarizes pH value of raw materials and biochar. The trend of graphics points out clearly that the biochar pH increases with increasing pyrolysis temperature. Many studies have shown that the increase in pH fluctuates with temperature.

The above takes place due to the increase in ash content and the change of oxygen function group during the thermochemical conversion of biomass[19]. However, the pH of the raw materials was significantly different, but in the production at two temperatures even biochar produced at the higher temperature has a slight pH increasing. This concludes that whatever the temperature selected to produce biochar, it gives an similar pH. which is alkaline (9.75-10.77). It would be suitable for acid soil improvement [17].

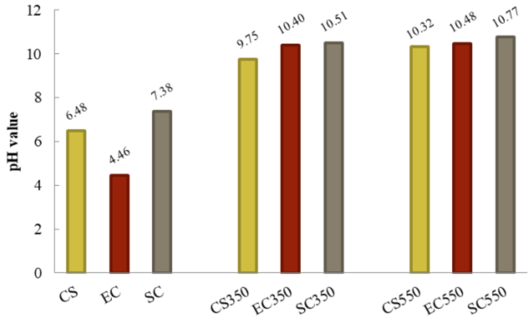

Fig.9. pH values of raw material and biochar

C. *Nutrient content*

The nutrient content may give a first indication on the suitability of fertilizer for soil amendment. The nutrient content of raw materials and biochar is shown in Table II. The separation of nutrients can be divided into two groups. First, main nutrients of chemical fertilizers are N, P, and K. Secondary nutrients content includes Ca, Mg and S. N present in biochar products has very poor accessibility, when compared with other nutrient content (Fig.10). The highest N content is found in sugarcane (0.59 %). This result showed the higher N content in raw materials than biochar product. The result may suggest that the biochar production during pyrolysis determined to a significant extent the N content. The greatest loss of N content at higher pyrolysis temperature[12].This reason leads to low N content in biochar product than raw materials.

Table II. Ultimate analysis and Nutrient Content of Raw Materials and Biochar

The happens with P content, it doesn't have a lot of

Samples	Ultimate analysis (%wt d.a.f.)				Nutrient content (%)						$\frac{P+K}{N}$
	C	H	N	O*	S	P	K	Ca	Mg	N	
CS	47.69	5.98	0.17	46.16	0.00	0.00	0.40	0.00	0.00	0.17	2.35
CS350	90.36	2.40	0.14	7.10	0.00	0.10	2.04	0.00	0.00	0.14	15.31
CS550	90.42	1.41	0.15	8.02	0.00	0.11	2.04	0.00	0.00	0.15	14.83
EC	45.19	6.34	0.11	48.36	0.00	0.00	0.58	0.71	0.00	0.11	5.53
EC350	87.97	2.66	0.26	9.11	0.13	0.18	2.43	2.03	0.18	0.25	10.64
EC550	90.21	1.57	0.13	8.09	0.09	0.17	2.74	3.02	0.22	0.12	24.25
SC	44.00	6.04	0.63	49.33	0.22	0.13	1.84	0.50	0.29	0.59	3.34
SC350	80.89	2.81	0.42	15.88	0.46	0.52	7.96	1.36	0.98	0.34	25.30
SC550	81.45	2.73	0.28	15.54	0.14	0.57	6.83	1.71	0.93	0.20	37.02

percentage but the trend is uptake when the temperature is high. The maximum value of P is 0.57 % that is found in SC 550. The most nutrient contents in all biochar's is K. The K values ranged from 41.58% to 89.47% of total nutrient content (N, P, K, Ca, Mg and S) and showed the highest content in SC350. Although the biochar product had lower N than raw material. However, using ratio of P and K is relative to N. The ratio used to identify the quality of biochar that they can act as The higher the ratio, the better the release of the nutrient fertilizer. In The Figure 11, those biochar the ratio is increasing with temperature. Therefore they can act as a slow release nutrient fertilizer.

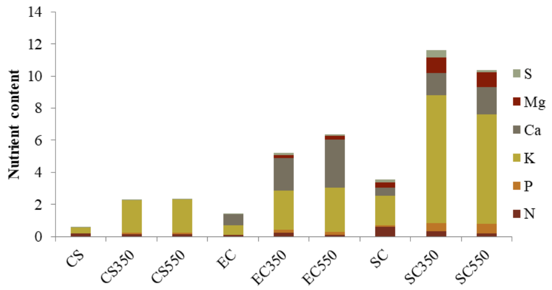

Fig.10. Percentage nutrients of contents of biomass and biochar

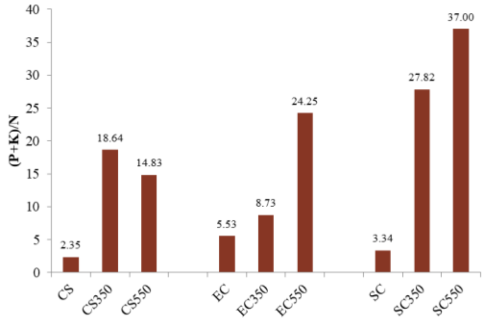

Fig.11. The ratio of P and K is relative to N of biomass and biochar

Mg and S showed the high value in SC350 of 0.98% and 0.46%, respectively. The highest Ca (3.02%) as found in EC550. Ca concentration shows clearly a trend related to the increasing of pyrolysis temperature. it can be concluded that biochar produced at high pyrolysis temperature (550°C) has higher Ca content than biochar produced at low temperature (350°C). The literature explained that typically large amounts of nutrients are lost via vaporization during pyrolysis with high temperature (exceeding 500 °C) [12]. Therefore, for the purpose of producing high nutrient contents and availability of biochar, it may be different for different raw materials, but it is preferable to keep the temperature below 400 °C [12]. This study concludes that the production of biochar with high nutrient contents must be produced at 350 °C. If necessary to produce biochar with specific type of nutrient content from different materials, the results might be the guideline to design pyrolysis temperature for biochar process.

The progress of this study was also monitored by Elemental compositions are presented in Table II. The carbon content increased with the temperature while oxygen and hydrogen were decreasing. The higher carbon content is found in coconut shell produced at 550 °C (90%).

However, considering the optimum point of production, the production of biochar from materials with high carbon content gives value yield less carbon in the production of biochar in the same conditions when compared with biochar produced from lower carbon content raw materials. In the case of biochar production at different temperatures, the results indicate that in the production of biochar from coconut shell (CS350 and CS550) given carbon content is 90.36% and 90.46%, respectively. The carbon content increased less than 1%. It can be concluded that 350°C is an optimum.

IV. Conclusion

This study investigated the effect of pyrolysis temperature on biochar quality for soil. Under pyrolysis temperature at 350 °C and 550°C pyrolysis was found to be an effective way to increase the biochar quality for soil. Biochar's characteristics were used to indicate the quality of biochar for soil in order to conclude whether surface area and total pore volume lead to high water holding capacity and can potentially increase the cation exchange capacity (CEC) of soils. Biochar produced from coconut shell at 550 °C (CS550) shows the highest surface area and total pore volume ($445 m^2/g$ and $0.22 cm^3/g$ respectively). Biochar's pH values are all alkaline (pH 9.88-10.77). Total nutrient content showed the highest value in sugar cane at 350°C. This study concludes that the production of biochar with high nutrient contents must be produced at 350 °C. The (P+K):N ratio was increasing with pyrolysis temperature. So biochar can act as a slow release nutrient fertilizer. However, this study can conclude that product biochar at 550 °C will have higher quality in terms of surface area, pore volume and (P+K):N ratio. These characteristics must be high value to use biochar for soil embedment. It is hoped that these findings will be a guideline to produce high quality biochar for soil improvement.

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